1986). A detailed characterization of the respective catalytically active species is to be published.

Our experimental findings allow the following conclusions: in a hydrogen atmosphere, the thermal degradation of metal carbonates, in particular of the naturally most abundant phase calcite, is observed at comparably low temperatures. This effect is enhanced by the admixture of selected transition metal carbonates. The evolved carbon compounds, carbon monoxide from pure alkaline-earth carbonates or methane from doped carbonates, give evidence for a different mechanism of the thermal degradations. The fact that the solid products not only represent potential catalysts for the conversion of CO_2 into organic carbon compounds with various possible products, but also act as effective CO_2-trapping systems, renders these systems interesting with respect to the problems arising from the increasing atmospheric CO_2 concentration[2-6].

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The stability of the fullerenes C_n, with $n = 24, 28, 32, 36, 50, 60$ and 70

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It has been proposed[1] that the geodesic and chemical properties inherent in a closed, hollow, spheroidal, carbon cage structure with the symmetry of a European football can readily explain the remarkable stability observed for the C_{60} molecule. Here I present a set of simple, empirical chemical and geodesic rules which relate the stability of carbon cages mainly to the disposition of pentagonal rings, or various directly fused pentagonal ring configurations. The rules yield cluster magic numbers consistent with observation and in particular predict that the fullerenes, C_n for which $n = 24$, 28, 32, 36, 50, 60 and 70 should have enhanced stability relative to near neighbours. These results provide further evidence for the proposal that closed hollow cages form when carbon nucleates in the vapour phase, and in particular that C_{60} buckminsterfullerene is indeed a truncated icosahedron as originally proposed[1].

It is now clear that the spectacular behaviour of C_{60} (ref. 1) observed in carbon nucleation studies using laser vaporization techniques[2] results from the inability of this species to take part in the general nucleation mechanism that produces large soot-like particles[3,4]. In the original study[1] it was suggested that a truncated icosahedral cage structure (Fig. 1) provides a simple explanation. Such a molecule was likely to be aromatic and able to survive the clustering process which leads to such soot-like particles because its closed spherical form imparts geodesic stability, as well as chemical inertness owing to the absence of the reactive sites that must occur at the edge of a flat graphite sheet. It was called buckminsterfullerene because the geodesic ideas associated with the constructs of Buckminster Fuller[5] had been instrumental in arriving at a plausible structure. It is convenient to retain this name for C_{60} and use the name fullerene generically for the class of all closed carbon cages composed of twelve 5-membered and an unrestricted number of 6-membered rings consistent with the constructs discussed in the original patents[5]. If necessary, conventional symmetry labels can also be used; for example, buckminsterfullerene is $(I_h)C_{60}$.

It was subsequently discovered that the C_{60} molecule had been postulated independently by several other workers[6-12]. In fact, an ingenious suggestion of Jones[11,12] which discusses hollow carbon molecules in general, predates these. Theoretical work since the initial discovery (see, for example, refs 13-19) has added significantly to the weight of evidence in favour of the suggested structure. The structural assignment rests on a range of circumstantial evidence which, taken in its entirety, makes a convincing case for a closed structure.

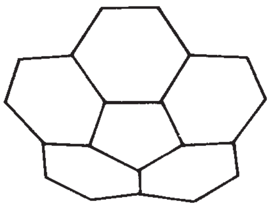
An important additional experimental observation is that, to a clear but lesser extent, enhanced stability is also shown by C_{70} and C_{50}[1,20,21]. Arguments that apply to C_{60} should also apply to C_{70} and C_{50} and thereby complement the case, albeit circumstantial, in favour of the closed-cage proposal[1].

A set of five basic empirical arguments can be presented to assess the relative stability of carbon cages.

(1) The networks should conform to the usual valence requirements of carbon, in that each atom should be three-connected to other atoms by one double and two single bonds. Thus, only even-numbered cages should be stable, and many resonance structures are desirable (in C_{60} there are 12,500 resonance structures[15]).

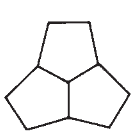
(2) Polyaromatic hydrocarbons with five - and six-membered rings are abundant, but three- and four-membered rings are very unstable and seven-membered ones rare. This suggests that only 5/6-ring networks are likely to occur readily. The cages must contain 12 pentagonal rings[12], but the number of hexagonal ones is not directly restricted.

(3) From Barth and Lawton's work[22] on the molecule corannulene (seen here in an edge-on perspective to highlight its non-planar saucer shape), it is clear that a structure in which a pentagon is completely surrounded by hexagons is stable. The simple molecule in which two pentagons are fused has not so far been made, although a stabilized analogue exists. These observations suggest that a cage in which all 12 pentagons are completely surrounded by hexagons has optimum stability and one in which pentagons abut is likely to be less stable. This argument can be carried further, in that closed structures involving various fused pentagon configurations are likely to exhibit varying degrees of strain-related instability. On this simple basis it is proposed that for the following configurations the local strain increases in order I→IV. Note that this set is not complete, as multiplet configurations in which pentagons abut sequentially, that is, share only one side, are not included. Such configurations are expected to exhibit stabilities intermediate between type II and type III.




I


II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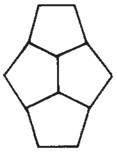
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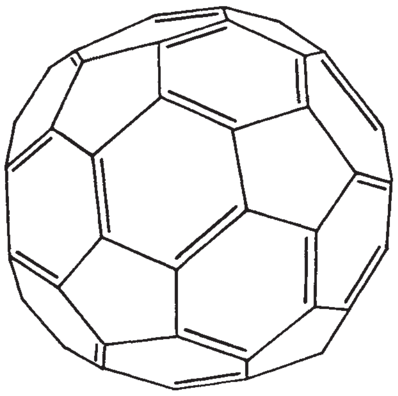

Fig. 1 The proposed structure of C_{60} buckminsterfullerene, the archetype of the fullerene family. It has *t*-icosahedral symmetry, as does the modern European football.

(4) Geodesic structural factors should favour the more symmetric isomers, which can evenly disperse the strain from bond-angle deformation. Structures in which curvature is localized or unevenly distributed are likely to be excessively strained and subject to attack at such positions.

(5) Closed-shell electronic structures are likely to be preferred. Fowler and Steer[19] have shown that cages with $60+6k$ atoms (where k is 0 or ≥ 2) can have a closed-shell electronic structure. The rule is not restrictive[19].

Any deductions based on such simple arguments are likely to be coloured by more subtle considerations but, leaving these aside for the moment, it is useful to see how far such simple arguments can go towards explaining the phenomena that have been observed so far.

C_{60}. C_{60} is the smallest closed network that can have all pentagons separated; that is, it involves only type-I configurations. It is thus the first highly strain-free cage capable of formation during clustering and as all 60 atoms are equivalent the strain energy is perfectly uniformly distributed. It should also have a closed-shell electronic configuration[19]. As C_{60} fulfills all the criteria above more perfectly than any other cluster—and, most importantly, is the first cage to form during clustering that can—it is expected to be the most stable and the dominant member of the fullerene family, as is observed.

C_{70}. It is not immediately obvious, but attempts to make model structures suggest that it is not possible to construct a closed network with separated pentagons again until the cluster has at least 70 atoms ((D_{5h})C_{70}, Fig. 2*a*). This conjecture has also been made independently by Schmalz *et al.*[14]. It is particularly satisfying that the rules, in their simplest form, explain both of the original observations[1]: the dominance of the C_{60} and the C_{70} signals.

C_{50}. Under gentle, one-photon F_2 excimer-laser ionization, C_{50} also appears special[20,21,23]. The necessity of having 12 pentagons in any closed cage[11,12] indicates that in this molecule some pentagons must abut. Again attempts to make model structures lead to the conclusion that C_{50} is the smallest cluster for which a cage can be constructed without triplets of directly (type-III) or sequentially fused pentagons; that is, type-I and II configurations suffice. Schmalz *et al.* have confirmed this conjecture using combinatoric relations[14]. One such 50-atom cluster, (D_{5h})C_{50}, is shown in Fig. 2*b*.

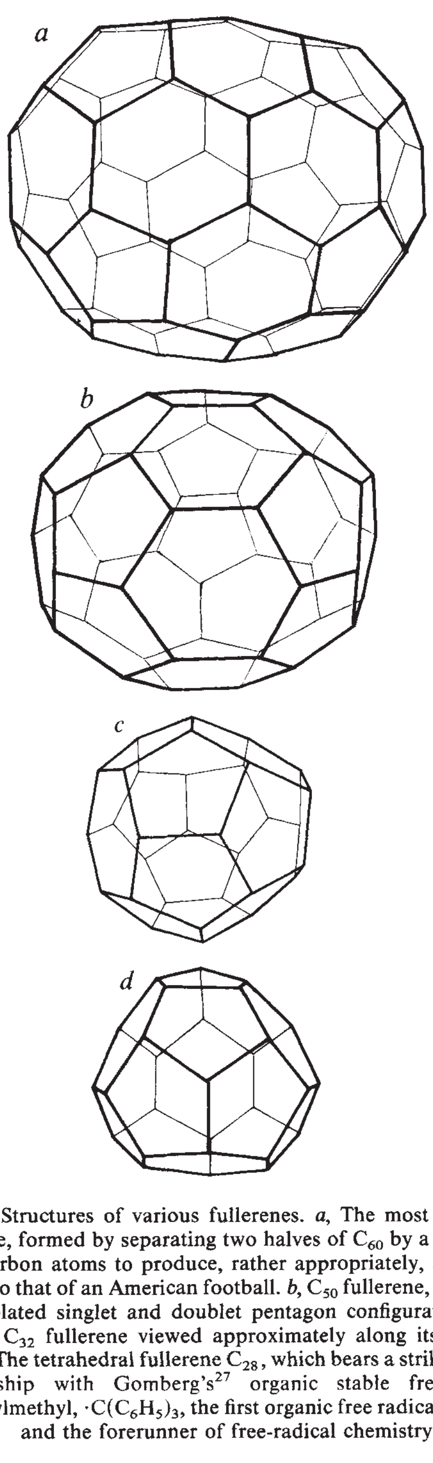

Fig. 2 Structures of various fullerenes. *a*, The most stable C_{70} fullerene, formed by separating two halves of C_{60} by a ring of ten extra carbon atoms to produce, rather appropriately, a structure similar to that of an American football. *b*, C_{50} fullerene, containing only isolated singlet and doublet pentagon configurations. *c*, A handed C_{32} fullerene viewed approximately along its threefold axis. *d*, The tetrahedral fullerene C_{28}, which bears a striking family relationship with Gomberg's[27] organic stable free radical, triphenylmethyl, $\cdot C(C_6H_5)_3$, the first organic free radical identified and the forerunner of free-radical chemistry.

C_{36}, C_{32}, C_{28}, C_{24} and C_{20}. It would appear[24] that all clusters with ≥ 36 atoms photo-fragment by eliminating two atoms at a time to produce the next-smaller even cluster. C_{34} appears to fragment by the loss of both two and three atoms at a time. C_{32} and smaller clusters seem to fragment almost completely into a range of small carbon fragments. The results of recent mass-spectrometric studies on carbon ions produced in hydrocarbon flames[25] are very interesting, in that not only are prominent peaks at 50, 60 and 70 observed but there appear to be no peaks lower than 32. These results are clear evidence for the validity of the proposed soot formation mechanism involving open, curved, graphitic shell embyros (refs 4, 3, 26; H.W.K. and K. McKay, to be published). They also suggest that hot clusters with less than 32 atoms may be particularly unstable under these conditions. Cages with less than 36 atoms appear to require the inclusion of some type-III or higher-order configurations in the network, and it seems reasonable to suppose that the discontinuity in the photo-fragmentation behaviour that occurs between C_{36} and C_{32} is a consequence of these structural limitations. The rules suggest that the most stable 32-atom cluster should be the rather interesting fullerene, (C_3)C_{32} (Fig. 2*c*), which involves only two type-III configurations and, incidentally, is handed. There does not appear to be a 30-atom cage that can avoid the inclusion of high-strain type-IV configurations, and it is thus quite reasonable to expect that multi-photon fragmentation of C_{32}, which must introduce large amounts of vibrational excitation into the cages, should show a discontinuity of the kind observed. There is, however, one even smaller cluster that can avoid type-IV configurations: the tetrahedral cluster $(T_d)C_{28}$ shown in Fig. 2*d*. This intriguing molecule consists of four linked, symmetrically disposed type-III configurations and four hexagonal faces. Its stability will depend on the ability of the spare electrons on the four carbon atoms at the centres of the four type-III configurations to stabilize by conjugation. C_{28} is not expected to be a closed-shell molecule (P. A. Fowler, personal communication). But it is interesting and perhaps significant, as far as stability is concerned, to note that this species is a rather neat condensed pseudo-tetramer of Gomberg's (J. R. Heath *et al.*, unpublished results) famous stable organic radical, triphenylmethyl, $\cdot C(C_6H_5)_3$, which was the first free radical to be positively identified, and was the species that initiated free-radical chemistry. It is highly likely that the methane-like analogue, $C_{28}H_4$, is stable. Note that there are clustering conditions that show the C_{28} cluster peak to be dominant when F_2 excimer radiation is used to ionize the cluster distribution[27]. Cox *et al.*[23] have also observed extra stability for C_{28}. At first sight it would seem that the out-of-plane distortion is too great and the cage network must have been deformed beyond breaking point to close such a structure involving sp^2-hybridized carbon. Carbon, however, appears able to break so many rules that one must continually reconsider them for this element. It is, after all, only after a great deal of study that the structures of even the smallest molecules such as C_2 and C_3 have been characterized and understood theoretically. Such studies urge caution in being too hasty with regard to assumptions about the electronic and geometric structure of carbon compounds in terms of conventional valence theory. Thus, one must seriously consider the possibility that the observed special behaviour of the C_{28} signal reflects the formation of the molecule shown in Fig. 2*d*, even though conventional wisdom would suggest that such a cage would be too strained to exist. The only other reasonable suggestion is that the cluster is linear; however, the evidence on the shorter linear chains[28,29] suggests that their magic-number sequence is not sensitive to the clustering conditions in the same way that the large even ones are. Finally, note that a closed C_{22} cage cannot be made[19], and that the most strained molecule must be C_{20}, which as it consists only of pentagons is the smallest fullerene that could exist. The large-even-cluster mass spectrum pattern of ref. 23 shows a clear break at C_{24}, with no evidence for C_{22} or C_{20}. It seems that under cool clustering conditions and very gentle ionization C_{24} is the smallest species that can be stable, whereas under high-temperature clustering conditions or high photon irradiation C_{32} is the smallest.

The large even clusters show stability across the whole range relative to the odd ones[4], suggesting that closure may be a general phenomenon. However, even the highly symmetric fullerenes are not expected to have closed electronic shells (P. A. Fowler, personal communication), although it is the case for C_{60} and C_{70}. Thus, just how significant the closed-shell requirement is remains an open question; in fact, the stability of Gomberg's triphenylmethyl suggests that it might not be as important as has been expected for graphitic networks. In addition, the fact that C_{60} shows special behaviour whether it is neutral or positively or negatively charged implies that the closed-shell requirement may not be a major criterion of stability in general. If this conclusion is correct then it may be because these systems are ideal delocalization networks for free electrons.

The approach described here can probably be developed further to include other possible fused pentagonal configurations and mixtures thereof. But more quantitative results would probably require a much more sophisticated approach, involving not only more detailed consideration of the bond-angle strain involved in closing up such networks but also other, more complicated problems such as electronic structure considerations. Some of these factors have been considered by various groups[14-19]. Nevertheless, the very simple arguments presented here appear to predict a special nature for C_{24}, C_{28}, C_{32}, C_{36}, C_{50}, C_{60} and C_{70}—species for which varying degrees of special behaviour have been observed. This is not an obvious magic number sequence and it would be very surprising if an alternative model that does not involve closed cages were able to arrive at the same set.

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Catalytic C–H bond activation on silicon dioxide overlayers

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The catalytic activation of hydrocarbon C–H bonds is a fundamental process in heterogeneous catalysis. Although C–H bonds are readily activated on certain metal surfaces, the nature of the catalytic sites is still not understood. Catalytic C–H bond activation with group VIII transition metals[1-7] is commonly studied by hydrogen/deuterium (H/D) exchange reactions of saturated hydrocarbons with D_2. These reactions have shown that the interconversion of Π-allyl intermediates is the most facile process leading to polydeuteration on platinum and rhodium[2-5]. Planar surfaces are the most active for C–H activation[4,5]. Carbonaceous

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